

2.2 Preparation and characterization nickel aluminate spinel via Sol-gel process.

As previously described, in the development of soft chemistry, the sol-gel process is considered to be the most chemical method for the synthesis of inorganic oxides. This process usually involves the hydrolysis and condensation of various metal alkoxide molecules under controlled conditions to form metal-oxygen-metal bridging units.

Due to the advantages of this process over the other existing chemical routes, including the potential to obtain ceramic materials exhibiting high purity, degree of homogeneity, porosity and specific surface area. Moreover yielding of this process is more controllable chemistry and minimizing special handling requirement. Therefore, the sol-gel process should be used to produce a homogeneous mesopore having high surface area.

In this work, nickel aluminate spinel was alternatively prepared by sol-gel process using nickel aluminate precursors obtained from the one pot synthesis. Due to pure nickel aluminate spinel was obtained when SPNO and SPAC were calcined, so SPNO and SPAC were selected in order to study the possibility to prepare nickel aluminate spinel via sol-gel process. The goal of this work was to study the appropriate conditions for preparation of nickel aluminate spinel from nickel aluminate precursors as a candidate precursor in sol-gel process. Additionally the influences of spinel precursor sources, concentrations, solvents, pH values and gelation temperatures on properties of nickel aluminate spinel were also investigated. In addition, some physical properties of NiAl_2O_4 obtained by the sol-gel technique are also observed and compared to those obtained directly by calcinations of the one pot synthesis product.

2.2.1 Study of gel formation for SPNO precursor

The gelation times of SPNO alcoholic precursor solution under varying concentrations and pH values were observed at room temperature ($\approx 30\text{ }^{\circ}\text{C}$) as well as at $60\text{ }^{\circ}\text{C}$. The results are summarized in Table 13 – 15. At room temperature, ethanolic precursor solution pH 6, polymeric gel formed rapidly, only the highest concentration studied, 32.0 % (w/v), however with increasing pH value, the initial concentration that able to form gel increased cover concentration range of 28.0 – 32.0 %, 24.0 – 32.0% and 20.0 – 32.0 % (w/v), for pH 7, 8 and 10, respectively (Table 13). Thus, it allowed to be concluded that the sequence of gel formation is pH 10.0 > 8.0 > 7.0 > 6.0. Noticeably, the systems with pH 9.0, showed the highest value of gelation times as comparing to others, because there were no addition of catalysis acid or base, Table 13.

The preference of gel formation at higher pH with concentration above 16 % (w/v) could be due to the effects of hydrolysis rate as well as hydrolysis ratio (h). Gel formation favors to occur at pH 10.0, with significantly decreasing to occur at lower pH. This could be described that the systems with higher pH having addition of base catalyst, molecular networks formed quickly via the reactions of hydrolysis and condensation. On the other hand, systems with lower pH having addition of acid catalyst, the hydrolysis reaction of SPNO precursor could be occurred very fast, leading to form precipitate. As increasing hydrolysis ratio or decreasing concentration of SPNO precursor, it reduced gel formation. It could be justified that when the hydrolysis ratio is greater, the $-M-OR$ groups composed in SPNO precursor are so strongly and quickly hydrolyzed and condensed through the reactions of hydrolysis and condensation, leading to form precipitate. On the other hand, systems with lower hydrolysis ratio or higher concentration, $-M-OR$ groups comprised in SPNO precursor are gradually hydrolyzed and followed by condensation and cross linking, so that polymeric gel was formed.

The SPNO precursor in n-propanol with concentration of 28.0 and 32.0 %(w/v) showed faster polymeric gel formation at pH 9.0 as comparing to the corresponding condition in ethanol (Table 13 - 14). When the temperature was increased to 60 °C, gel formation occurs faster because SPNO precursor molecules move more rapidly and frequently collide, so the reaction rate is increased, resulting in a shorter gelation time.

From the above experiments, SPNO alcoholic precursor solution favorably to form gel in ethanol (Table 13) and rarely form gel in n-propanol (table 14) whereas in i-propanol, it is unable to form gel in all systems (Table 15), thus it allowed to conclude that the ease of gel formation in alcohol solution is in the order of ethanol > n-propanol > i-propanol.

It is basically considered to be due to the easy exchange of ethoxide groups ($-\text{OCH}_2\text{CH}_3$) in ethanol with the alkoxide groups ($-\text{M}-\text{OR}$) of SPNO precursor through solvent exchange process, which allowed alkoxide groups to be hydrolyzed and condensed to form gel. On the contrary, the exchangeabilities of n-propoxide groups ($-\text{OCH}_2\text{CH}_2\text{CH}_3$) and i-propoxide groups [$-\text{OCH}(\text{CH}_3)_2$] are rather difficult because they are quite bulky, thus alkoxide groups in SPNO precursor were hydrolyzed so fast to form precipitate.

Table 13 Gelation time observed at room temperature and 60 °C for SPNO precursor dissolved in ethanol with various concentrations and pH values.

pH	Conc. (%w/v)	Room temperature		60 °C	
		Observation	Gel time (h)	Observation	Gel time (h)
6.0	16.0	P	-	P	-
	20.0	P	-	P	-
	24.0	P	-	P	-
	28.0	P	-	P	-
	32.0	G	0	-	-
7.0	16.0	P	-	P	-
	20.0	P	-	P	-
	24.0	P	-	P	-
	28.0	G	0	-	-
	32.0	G	0	-	-
8.0	16.0	P	-	P	-
	20.0	P	-	P	-
	24.0	G	0	-	-
	28.0	G	0	-	-
	32.0	G	0	-	-
9.0	16.0	P	-	P	-
	20.0	P	-	P	-
	24.0	G	2.50	G	1.25
	28.0	G	864	G	58.25
	32.0	G	960	G	172.25
10.0	16.0	P	-	P	-
	20.0	G	0	-	-
	24.0	G	0	-	-
	28.0	G	0	-	-
	32.0	G	0	-	-

Abbreviation: P = precipitate, G = gel

Table 14 Gelation time observed at room temperature and 60 °C for SPNO precursor dissolved in n-propanol with various concentrations and pH values.

pH	Conc.(%w/v)	Room temperature		60 °C	
		Observation	Gel time (h)	Observation	Gel time (h)
6.0	16.0	P	-	P	-
	20.0	P	-	P	-
	24.0	P	-	P	-
	28.0	P	-	P	-
	32.0	P	-	P	-
7.0	16.0	P	-	P	-
	20.0	P	-	P	-
	24.0	P	-	P	-
	28.0	P	-	P	-
	32.0	P	-	P	-
8.0	16.0	P	-	P	-
	20.0	P	-	P	-
	24.0	P	-	P	-
	28.0	P	-	P	-
	32.0	P	-	P	-
9.0	16.0	P	-	P	-
	20.0	P	-	P	-
	24.0	P	-	P	-
	28.0	G	0	-	-
	32.0	G	24	G	4
10.0	16.0	P	-	P	-
	20.0	P	-	P	-
	24.0	P	-	P	-
	28.0	P	-	P	-
	32.0	P	-	P	-

Abbreviation: P = precipitate, G = gel

Table 15 Gelation time observed at room temperature and 60 °C for SPNO precursor dissolved in i-propanol with various concentrations and pH values.

pH	Conc. (%w/v)	Room temperature		60 °C	
		Observation	Gel time (h)	Observation	Gel time (h)
6.0	16.0	P	-	P	-
	20.0	P	-	P	-
	24.0	P	-	P	-
	28.0	P	-	P	-
	32.0	P	-	P	-
7.0	16.0	P	-	P	-
	20.0	P	-	P	-
	24.0	P	-	P	-
	28.0	P	-	P	-
	32.0	P	-	P	-
8.0	16.0	P	-	P	-
	20.0	P	-	P	-
	24.0	P	-	P	-
	28.0	P	-	P	-
	32.0	P	-	P	-
9.0	16.0	P	-	P	-
	20.0	P	-	P	-
	24.0	P	-	P	-
	28.0	P	-	P	-
	32.0	P	-	P	-
10.0	16.0	P	-	P	-
	20.0	P	-	P	-
	24.0	P	-	P	-
	28.0	P	-	P	-
	32.0	P	-	P	-

Abbreviation: P = precipitate, G = gel

2.2.2 Study of gel formation for SPAC precursor

The behavior of SPAC is not similar to the typical SPNO precursor source because gel formation occurred in neutral solution, pH 7.0 in all types of alcohol studied; moreover it occurred in a slight basic solution of i-propanol at pH 8.0. Furthermore, gel is more likely to form at higher temperature in ethanol and n-propanol solvents, which was contrary to i-propanol, except that for pH 8.0 with concentration of 20.0 %(w/v), Table 16 – 18. A very short gelation time shown gel rapidly formed for concentrations of 20.0 – 32.0 %(w/v), implies that the appropriate conditions to form polymeric gel for SPAC precursor is in the solution of i-propanol with the concentration range of 20.0 – 32.0 %(w/v), pH 7.0 (Table 18). Due to a difficulty of solvent exchange in the system of i-propanol, therefore it allowed the presence alkoxide groups in SPAC precursor to be frequently hydrolyzed and increased in water and/or alcohol condensation for cross-linking to form gel. The preference of gel formation at lower pH could be resulted from the addition of large amount of acid catalyst in the strong basic solution of SPAC solution (initial pH value of alcoholic SPAC solution is 11).

At lower concentration observed, gel formation appeared to be low gelation time value, this result can be elucidated that at lower concentration revealed a high hydrolysis ratio, so that the –M-OR groups composed in SPAC precursor are rapidly hydrolyzed leading to form gel at a very short gelation time whereas at higher concentration, gel formation showed high gelation time value possibly due to a low hydrolysis ratio, thus –M-OR groups comprised in SPAC precursor are slowly hydrolyzed leading to form polymeric gel at a very long gelation time.

The gelation temperatures were also studied, it can be elucidated that at 60 °C gel formation occurs faster, resulting in a short gelation time. This could be explained in the same reason as gel formation for SPNO precursor.

Table 16 Gelation time observed at room temperature and 60 °C for SPAC precursor dissolved in ethanol with various concentrations and pH values.

pH	Conc. (%w/v)	Room temperature		60 °C	
		Observation	Gel time (h)	Observation	Gel time (h)
7.0	16.0	-	-	G	4
	20.0	-	-	G	16
	24.0	-	-	G	24.25
	28.0	-	-	-	-
	32.0	-	-	-	-
8.0	16.0	-	-	-	-
	20.0	-	-	-	-
	24.0	-	-	-	-
	28.0	-	-	-	-
	32.0	-	-	-	-
9.0	16.0	-	-	-	-
	20.0	-	-	-	-
	24.0	-	-	-	-
	28.0	-	-	-	-
	32.0	-	-	-	-
10.0	16.0	-	-	-	-
	20.0	-	-	-	-
	24.0	-	-	-	-
	28.0	-	-	-	-
	32.0	-	-	-	-
11.0	16.0	-	-	-	-
	20.0	-	-	-	-
	24.0	-	-	-	-
	28.0	-	-	-	-
	32.0	-	-	-	-

Abbreviation: P = precipitate, G = gel

Table 17 Gelation time observed at room temperature and 60 °C for SPAC precursor dissolved in n-propanol with various concentrations and pH values.

pH	Conc. (%w/v)	Room temperature		60 °C	
		Observation	Gel time (h)	Observation	Gel time (h)
7.0	16.0	P	-	P	-
	20.0	G	360	G	8.30
	24.0	G	696	G	32
	28.0	-	-	-	-
	32.0	-	-	-	-
8.0	16.0	-	-	-	-
	20.0	-	-	-	-
	24.0	-	-	-	-
	28.0	-	-	-	-
	32.0	-	-	-	-
9.0	16.0	-	-	-	-
	20.0	-	-	-	-
	24.0	-	-	-	-
	28.0	-	-	-	-
	32.0	-	-	-	-
10.0	16.0	-	-	-	-
	20.0	-	-	-	-
	24.0	-	-	-	-
	28.0	-	-	-	-
	32.0	-	-	-	-
11.0	16.0	-	-	-	-
	20.0	-	-	-	-
	24.0	-	-	-	-
	28.0	-	-	-	-
	32.0	-	-	-	-

Abbreviation: P = precipitate, G = gel

Table 18 Gelation time observed at room temperature and 60 °C for SPAC precursor dissolved in i-propanol with various concentrations and pH values.

pH	Conc. (%w/v)	Room temperature		60 °C	
		Observation	Gel time (h)	Observation	Gel time (h)
7.0	16.0	P	-	P	-
	20.0	G	0	-	-
	24.0	G	0	-	-
	28.0	G	0	-	-
	32.0	G	0	-	-
8.0	16.0	G	0	-	-
	20.0	G	24	G	8
	24.0	-	-	G	34.50
	28.0	-	-	-	-
	32.0	-	-	-	-
9.0	16.0	-	-	-	-
	20.0	-	-	-	-
	24.0	-	-	-	-
	28.0	-	-	-	-
	32.0	-	-	-	-
10.0	16.0	-	-	-	-
	20.0	-	-	-	-
	24.0	-	-	-	-
	28.0	-	-	-	-
	32.0	-	-	-	-
11.0	16.0	-	-	-	-
	20.0	-	-	-	-
	24.0	-	-	-	-
	28.0	-	-	-	-
	32.0	-	-	-	-

Abbreviation: P = precipitate, G = gel

2.2.3 XRD analysis of pyrolyzed SPNO gel

Some preliminary studies of calcined gel products at 1000°C for 5 h were investigated by XRD technique. After calcined gel that occurred at room temperature for the series of 32 % (w/v) of SPNO precursor solution in ethanol with varying pH values from 6.0 to 10.0, the XRD patterns of the obtained powders are similar and shown identical in peak positions as illustrated in Figure 12 (a) – (e). The calcined products exhibited sharp peaks of NiAl₂O₄ phase indicating by the major peaks at 311, 400 and 440 *hkl* reflections corresponding to the JCPDS file No. 10-0339 and small peaks of NiO phase as compared to the JCPDF file No. 44 – 1159. Pyrolysis of gel which obtained from other SPNO precursor concentrations and pH values revealed the same XRD patterns of the products as compared to those obtained from gel at 32.0 % (w/v) (see Appendix E, Figure E14 – Figure E19).

However, closed examination of X-ray diffraction pattern, it demonstrates the relation of NiO peak intensities to gelation time. As obviously seen in the systems of ethanolic precursor solution at room temperature, pH 9.0, The XRD pattern of pyrolyzed gel obtained from 24.0, 28.0 and 32.0 % (w/v), with the gelation time values of 2.50, 864 and 960 hours, respectively; (Table 13), showed that as gelation time increased, the intensities of NiO phase increased (see Figure 13). The fact that high amount of NiO phase found in the samples which have high gelation time may be due to the nucleation and crystal growth of NiO phase greater occur during the gel formation. It is worth to note that the purity of pyrolysed SPNO gel increased with decreasing gelation time.

Similarly, the XRD patterns of pyrolyzed gel occurring in the n-propanolic and i-propanolic solutions showed the same pattern as presented for gel in ethanol (see Appendix E, Figure E20 – Figure E21).

By comparing XRD results for gel calcined at 1000 °C for 5 h and step calcination (500 °C for 5 and held at 1000 °C for 5 h), it was found that both conditions illustrated identical X-ray diffraction patterns for all systems of gel formation, see Appendix E, Figure E14 – Figure E21).

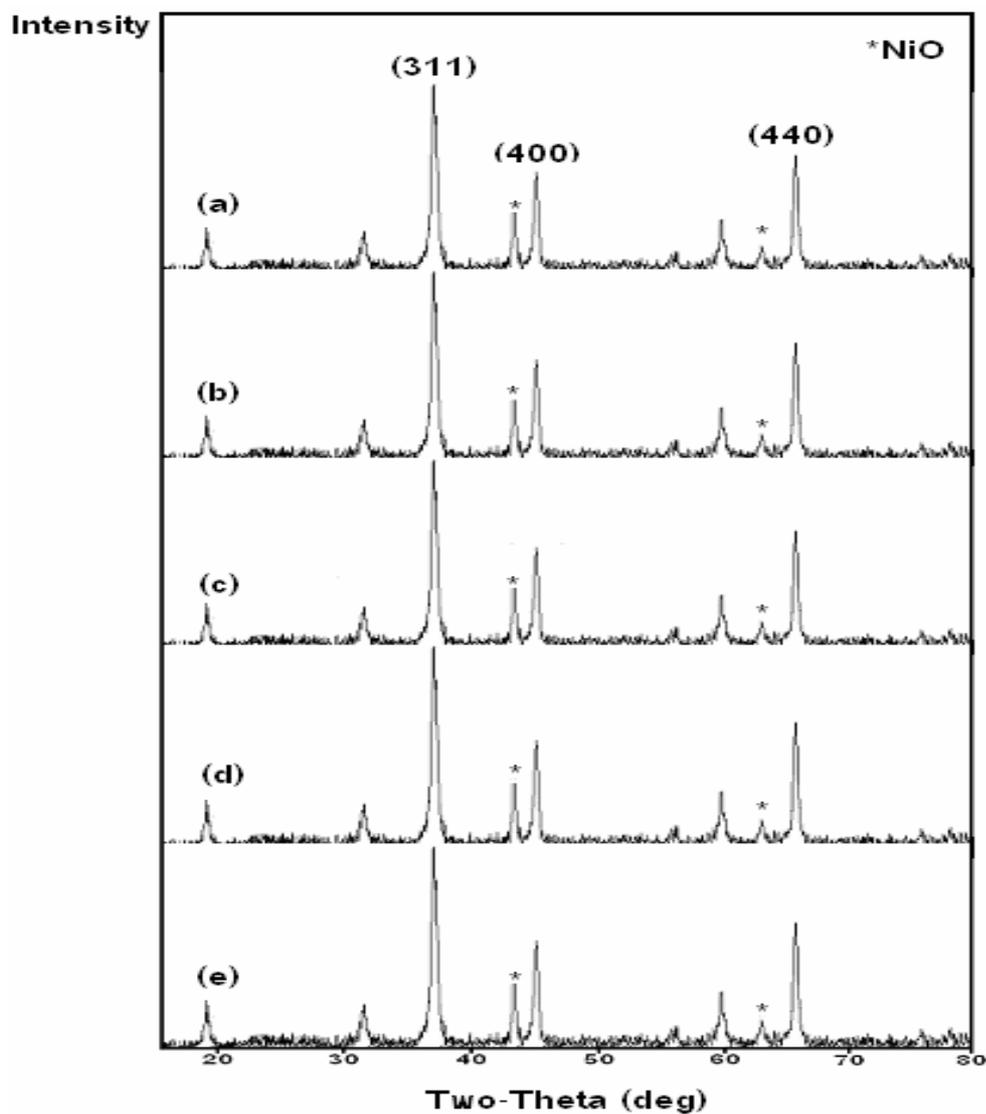


Figure 12 X-ray diffraction patterns of the powder obtained from 1000 °C (5 h) pyrolysis of gel occurring at room temperature for SPNO precursor in 32.0 % (w/v) ethanolic solution with various pH values; (a) 6.0, (b) 7.0, (c) 8.0, (d) 9.0 and (e) 10.0

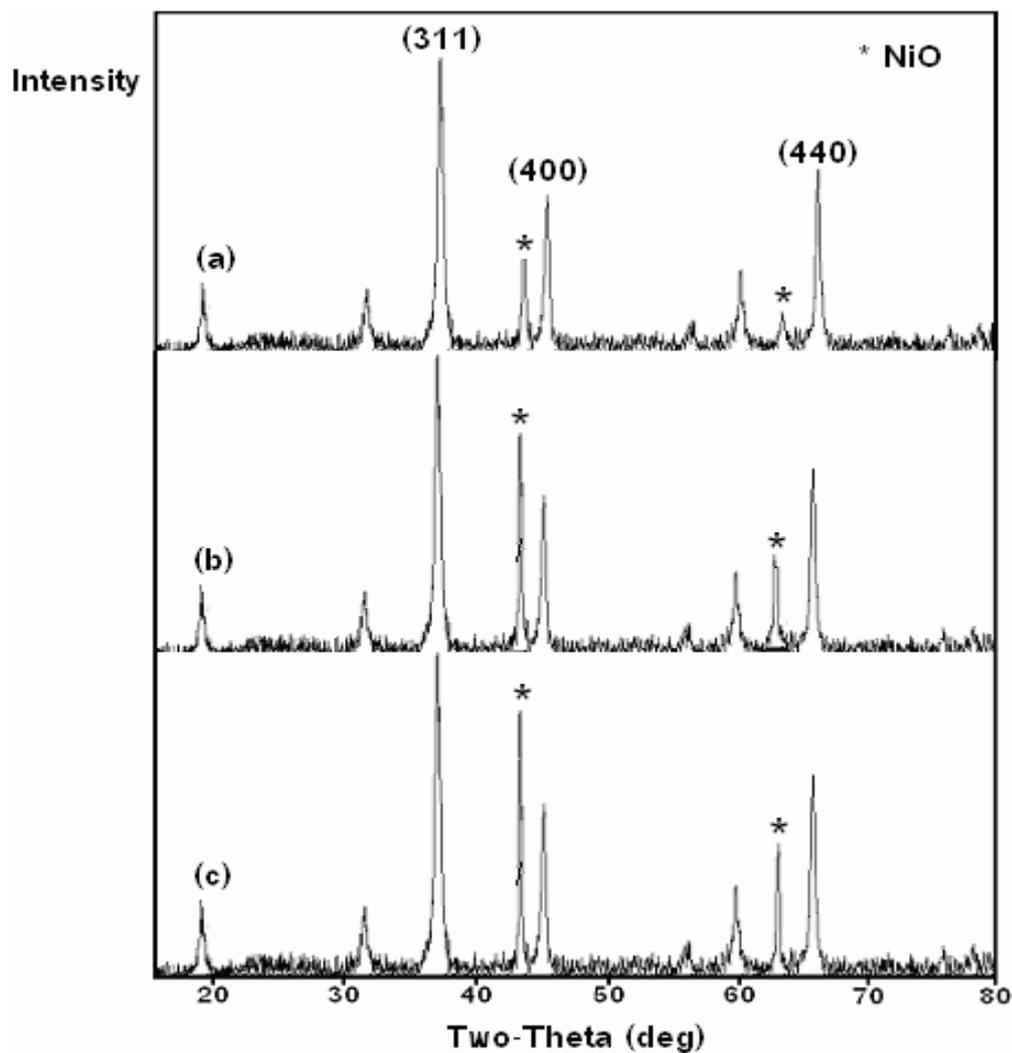


Figure 13 X-ray diffraction pattern of the powder obtained from 1000 °C (5 h) pyrolysis of gel occurring at room temperature, pH 9.0, in the ethanolic solution of SPNO precursor with different concentrations and gelation times; (a) 24.0 % (w/v), 2.5 h (b) 28.0 % (w/v), 864 h and (c) 32.0 % (w/v), 960 h.

2.2.4 XRD analysis of pyrolyzed SPAC gel

The X-ray diffraction patterns of the powders obtained from gel occurred at room temperature in the i-propanolic solution of SPAC precursor, pH 7.0 with precursor concentrations ranging from 20.0 – 32.0 % (w/v) and calcined at 1000 °C for

5 h in air as illustrated in Figure 14 are similar and show the same peak positions of NiAl_2O_4 phase mixed with NiO phase. For other pH values with various precursor concentrations, XRD patterns of the powders are equivalent to that of the powders obtained from gel at pH 7.0 which prepared in the same methodology (see Appendix E, Figure E25 – Figure E27).

XRD results for NiAl_2O_4 spinel powders obtained from gel occurring in the ethanol and n-propanolic solutions of SPAC precursor as shown in Appendix E, Figure E22 – Figure E24 are similar to those previously presented for i-propanolic solutions which consist of NiAl_2O_4 spinel and NiO phases.

The XRD results of NiAl_2O_4 spinel powders obtained from gel calcined at $500\text{ }^\circ\text{C}$ for 5 and held at $1000\text{ }^\circ\text{C}$ for 5 h following sol-gel processing at all conditions are shown in Appendix E, Figure E22 – Figure E27. All of peak positions in the spectra showed the same peak positions of NiAl_2O_4 spinel powders obtained from gel calcined at $1000\text{ }^\circ\text{C}$ for 5 h which involved mixed phases of NiAl_2O_4 spinel and NiO.

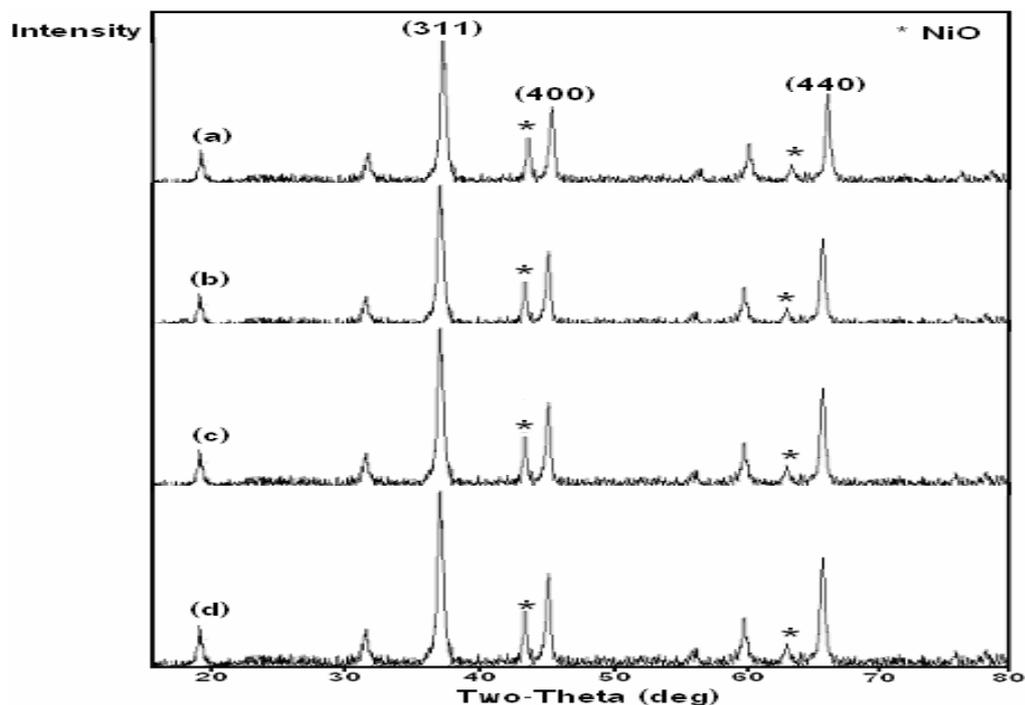


Figure 14 X-ray diffraction pattern of the powder obtained from 1000 °C (5 h) pyrolysis of gel occurring at room temperature, pH 7.0, in the i-propanolic solution of SPAc precursor with different concentrations; (a) 20.0 % (w/v), (b) 24.0 % (w/v), (c) 28.0 % (w/v) and (d) 32.0 % (w/v)

2.2.5 Comparison XRD pattern of NiAl_2O_4 powders obtained by different preparation methods

The XRD patterns of the resulting products obtained by different methods are compared and shown in Figure 15. The XRD patterns of the powders which prepared by a direct calcination of SPNO and SPAc, exhibited single NiAl_2O_4 phase and consistent with that synthesized by coprecipitation method (Cesteros *et al.*, 2000). Two phases of NiAl_2O_4 and NiO were observed for the powders prepared via sol-gel process. Due to the nucleation and crystal growth of NiO phase occur in the gel formation, therefore it allowed the presence NiO phase in samples obtained by sol-gel method.

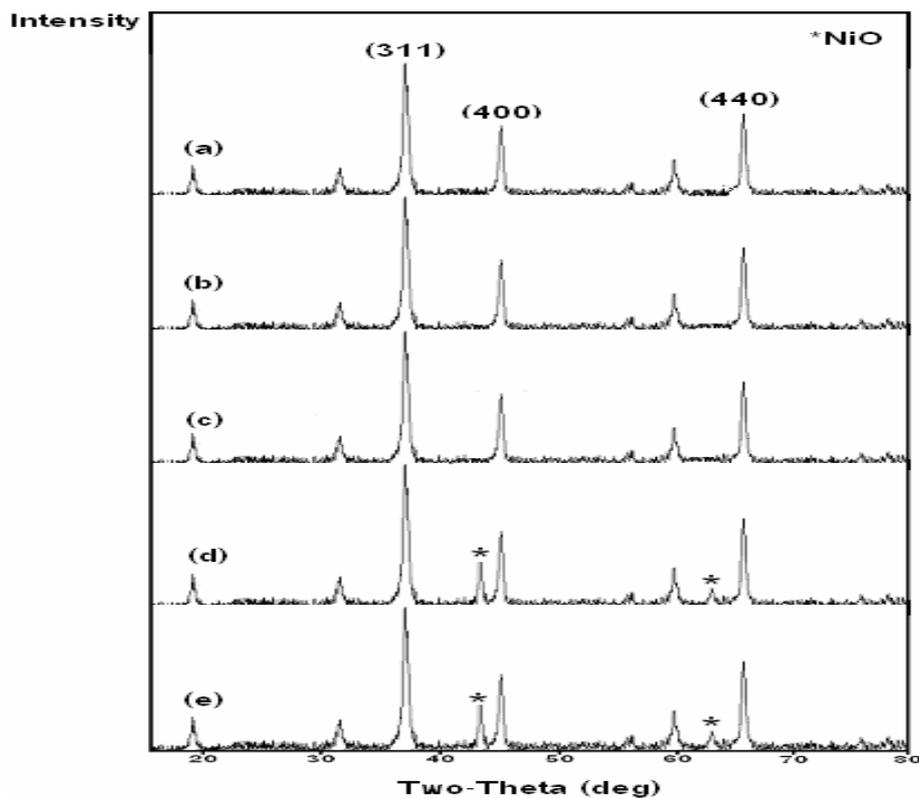


Figure 15 XRD patterns of NiAl_2O_4 spinels prepared by different preparation methods and heat at 1000°C for 5 h in air: (a) coprecipitation (Cesteros *et al.*, 2000), (b) directly calcined SPNO precursor, (c) directly calcined SPAC precursor, (d) SPNO sol-gel and (e) SPAC sol-gel.

2.2.6 Effect of sol-gel process to spinel morphology for SPNO gel

The microstructure of the NiAl_2O_4 powders produced from gel was determined by Scanning Electron Microscope. Figures 16 - 20 show typical SEM micrographs of pyrolyzed SPNO gel which formed in 32.0 % (w/v) ethanolic solution, pH 6.0 – 10.0, at room temperature. For gels pyrolyzed at 1000°C , the microstructures of the powders obtained from gel at pH 6.0 (Figure 16 (a)) and pH 8.0 (Figure 18 (a)) were made up of more uniform, spherical particles with grain sizes ranging from 100 – 150 nm, but the former powder showed a higher porous structure with the presence of large pores between particles. The powder resulted from gel at pH 7.0 (Figure 17 (a)) was

denser and there are smaller particles size distribution on the agglomerated ones. The particles of the NiAl_2O_4 prepared by pyrolysing gel forming at pH 9.0 (Figure 19 (a)), were irregular block-like with large pores between particles and it showed the distribution of several numbers of small NiO particles because this condition has the highest gelation time value (960 h), this result is in agreement with the XRD result, Figure 13 (c). The densest structure with no pore was found in calcined gel of pH 10.0 as shown in Figure 20 (a).

Microstructure of powders heated at $1000\text{ }^\circ\text{C}$ for 5 h and those heated at $500\text{ }^\circ\text{C}$ for 5 h then continues heating at $1000\text{ }^\circ\text{C}$ for 5 h are compared. Gel products calcined at $500\text{ }^\circ\text{C}$ and held at $1000\text{ }^\circ\text{C}$ for 5 h showed more agglomerates and became denser than those at $1000\text{ }^\circ\text{C}$, Figure 16 (b) – 20 (b).

Effect of solvent on microstructure was shown as seen in Appendix F, Figure F13 – Figure F15, the morphology of NiAl_2O_4 obtained from gel in n-propanol, was rather nonuniform and has a small number of pores between particles which are different from those in ethanol.

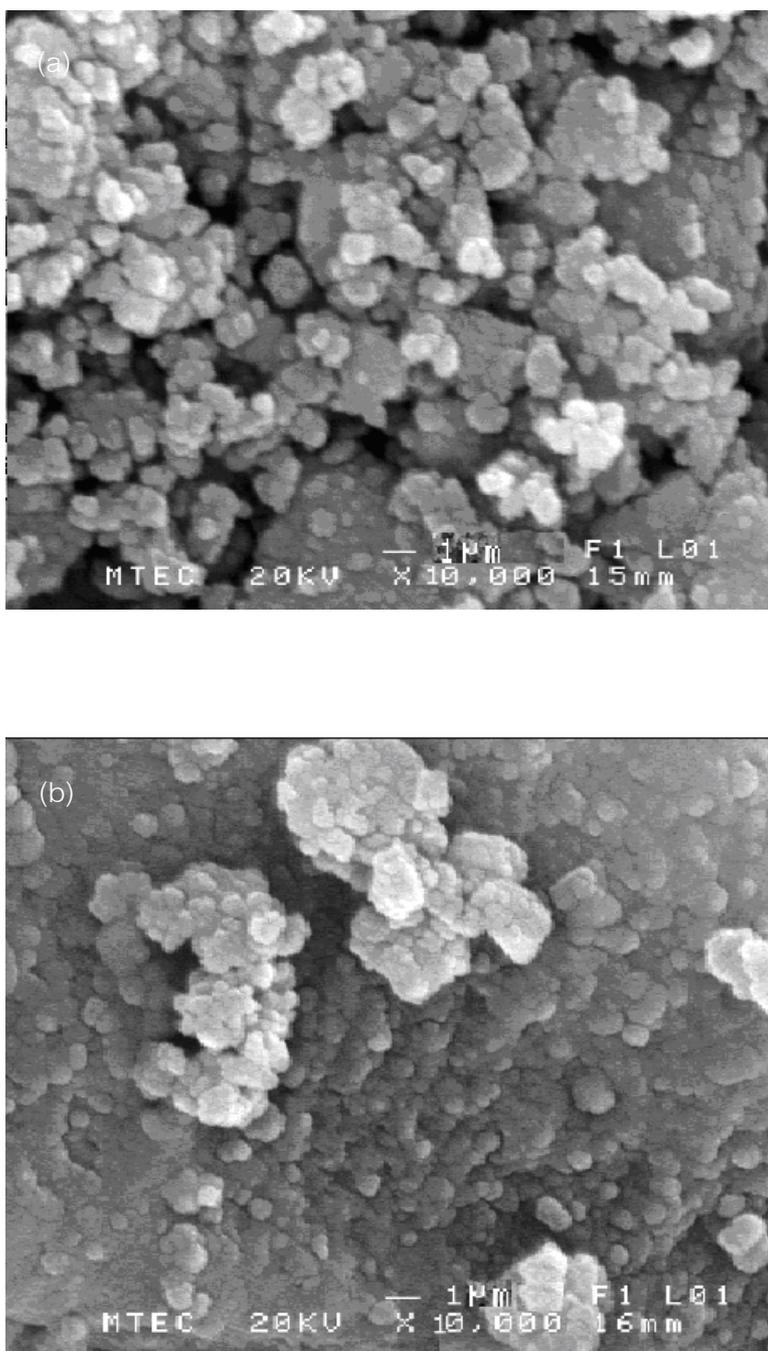


Figure 16 SEM micrographs of the NiAl_2O_4 powder obtained from gel occurring at room temperature in the system of 32.0 % (w/v) in ethanolic solution of SPNO precursor with pH 6.0 and calcination at different conditions: (a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h. The magnification (10,000x) is the same for all pictures.

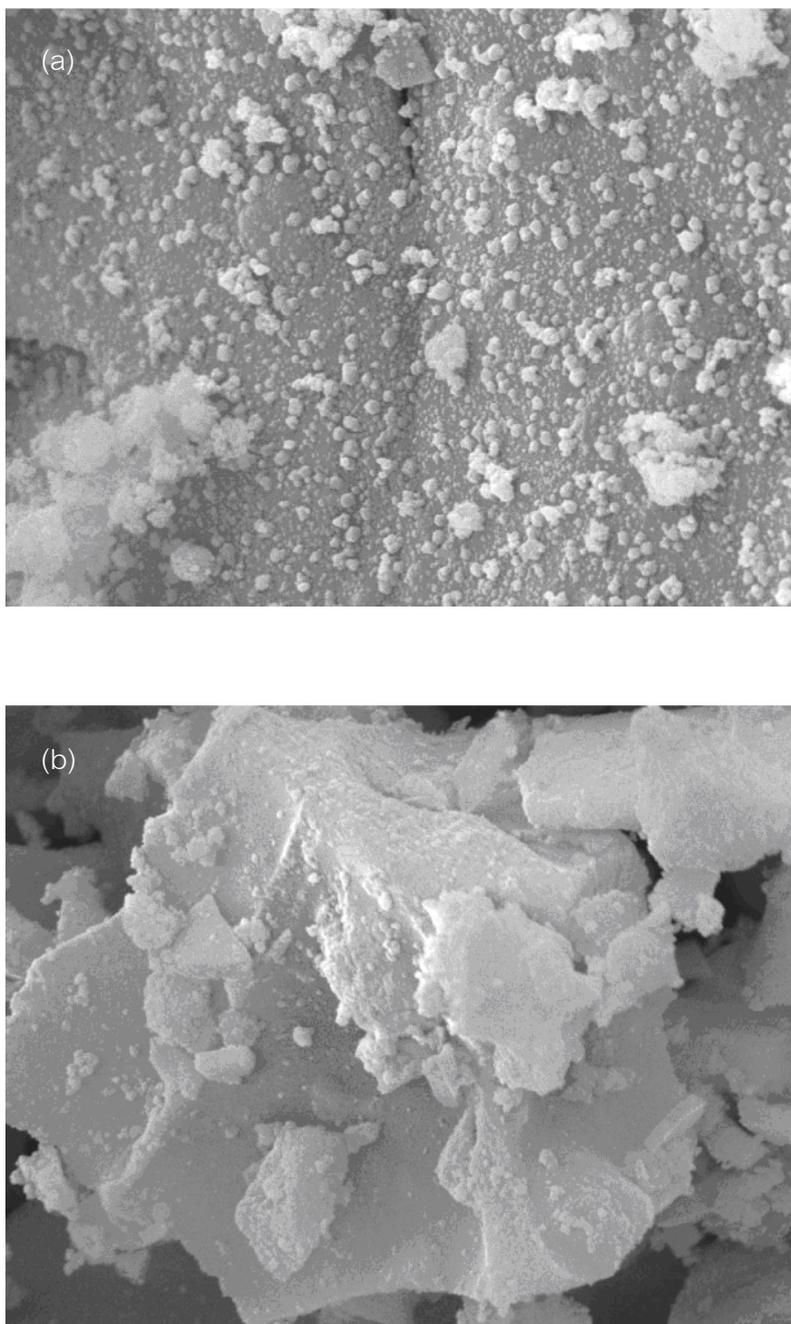


Figure 17 SEM micrographs of the NiAl_2O_4 powder obtained from gel occurring at room temperature in the system of 32.0 % (w/v) in ethanolic solution of SPNO precursor with pH 7.0 and calcination at different conditions: (a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h. The magnification (10,000x) is the same for all pictures.

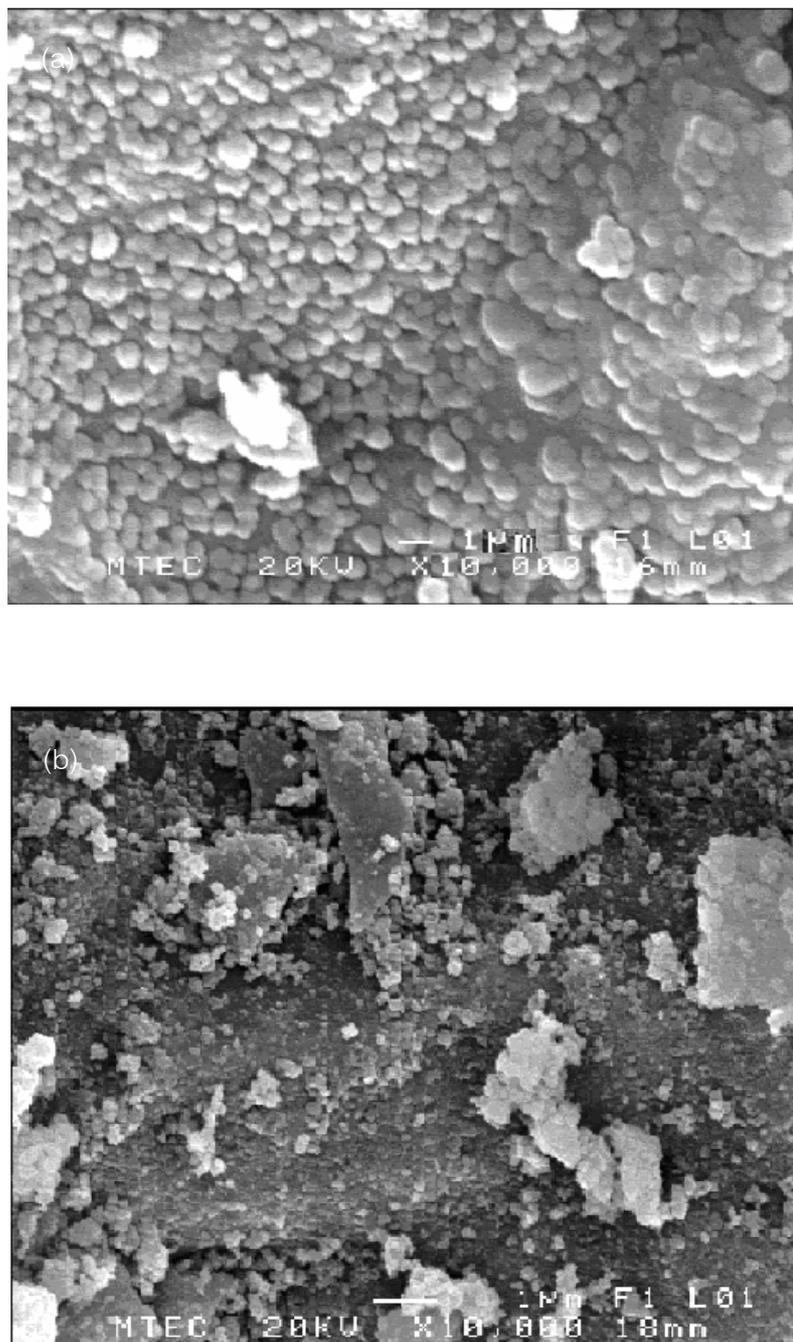


Figure 18 SEM micrographs of the NiAl_2O_4 powder obtained from gel occurring at room temperature in the system of 32.0 % (w/v) in ethanolic solution of SPNO precursor with pH 8.0 and calcination at different conditions: (a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h. The magnification (10,000x) is the same for all pictures.

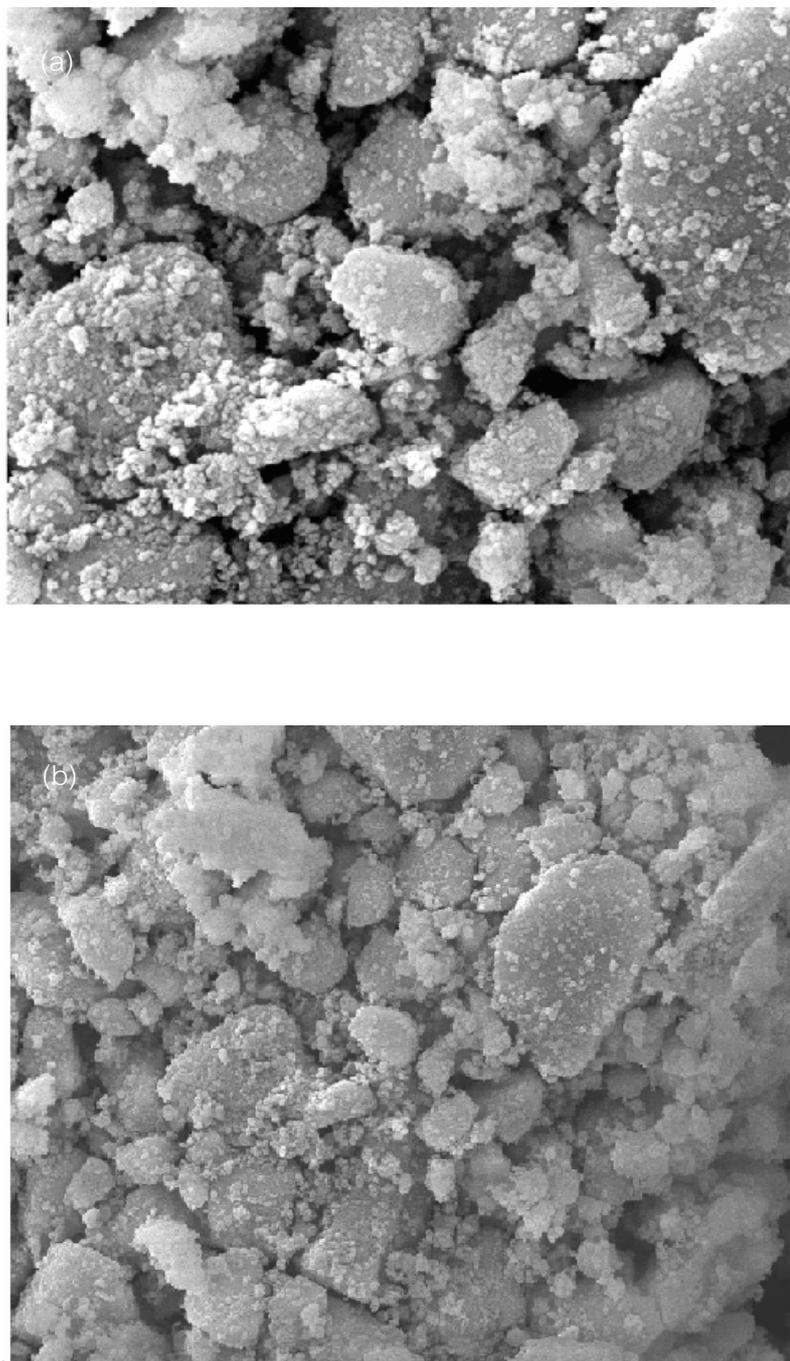


Figure 19 SEM micrographs of the NiAl₂O₄ powder obtained from gel occurring at room temperature in the system of 32.0 % (w/v) in ethanolic solution of SPNO precursor with pH 9.0 and calcination at different conditions: (a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h. The magnification (10,000x) is the same for all pictures.

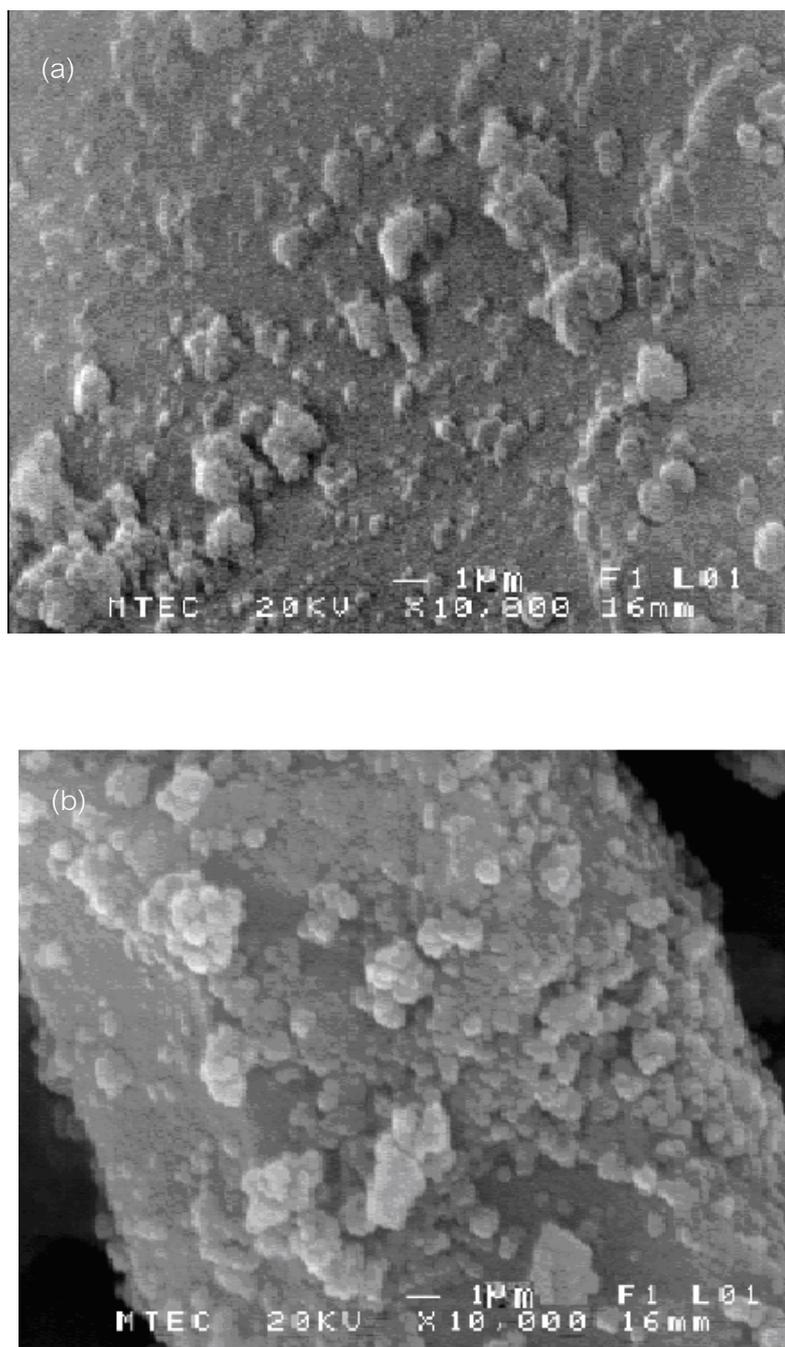


Figure 20 SEM micrographs of the NiAl_2O_4 powder obtained from gel occurring at room temperature in the system of 32.0 % (w/v) in ethanolic solution of SPNO precursor with pH 10.0 and calcination at different conditions:
(a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.
The magnification (10,000x) is the same for all pictures.

2.2.7 Effect of sol-gel process to spinel morphology for SPAc gel

To give the information about microstructure and morphology of NiAl_2O_4 prepared by sol-gel method, typical SEM micrographs of powders obtained from pyrolysis of SPAc gel occurring in the systems of 16.0 % (w/v) at room temperature including 20.0 – 24.0 % (w/v) at 60 °C in i-propanolic solution, pH 8.0 and heated at 1000 °C for 5 h in air were shown in Figure 21 (a) – 23 (a). From the SEM observation of Figure 21 (a), the calcined product obtained from gel occurring in 16.0 % (w/v) showed well faceted grains made up of several tiny spherical particles. The powder resulted from gel in 20.0 % (w/v) showed nearly spherical particles in some area whereas agglomerates of nonuniform particles still observed in surface of NiAl_2O_4 powder as seen in Figure 22 (a). The densest structure with smallest particles was observed for NiAl_2O_4 spinels obtained from gel occurring in 24.0 % (w/v) as shown in Figure 23 (a).

Comparing the morphology of the NiAl_2O_4 spinel powders obtained from step calcinations (500 °C for 5 h and held at 1000 °C for 5 h) with non step calcinations (1000 °C for 5 h) are studied. As shown in Figure 21 (b), the SEM micrograph of the step calcined products obtained from gel in 16.0 % (w/v) indicated that the particles begin to agglomerate together and became denser structure with smaller particles on the agglomerated ones. However, the powder resulted from gel in 20.0 % (w/v) form uniform morphology with small spherical particles and showed a porous structure with the existence of large pores between particles as shown in Figure 22 (b). Similarly, the SEM micrograph of step calcined gel occurring in 24.0 % (w/v) showed the dense microstructure as presented for non step calcined gel but the former powder showed bigger particles size dispersion on agglomerated ones (see Figure 23 (b)).

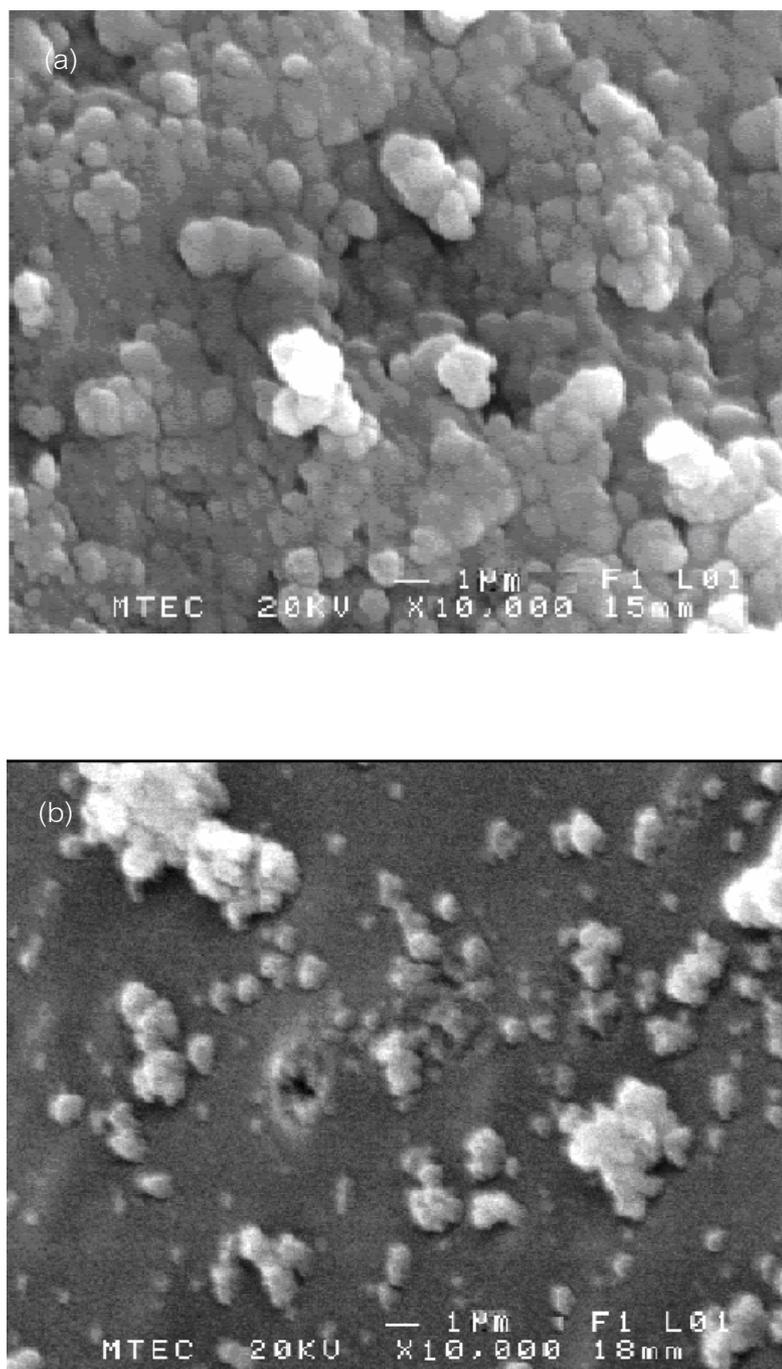


Figure 21 SEM micrographs of the NiAl_2O_4 powder obtained from gel occurring at room temperature in the system of 16.0 % (w/v) in i-propanolic solution of SPAC precursor with pH 8.0 and calcination at different conditions:
(a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.
The magnification (10,000x) is the same for all pictures.

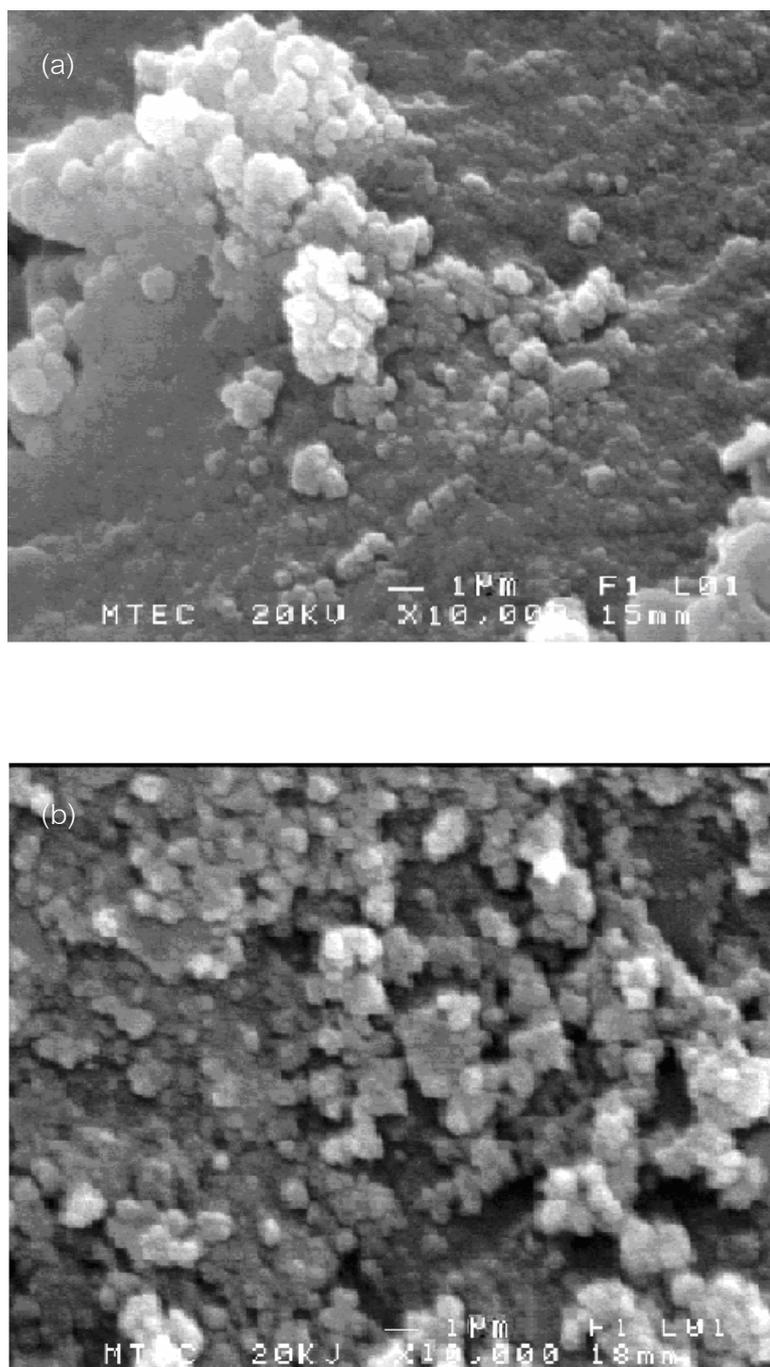


Figure 22 SEM micrographs of the NiAl_2O_4 powder obtained from gel occurring at 60°C in the system of 20.0 % (w/v) in i-propanolic solution of SPAc precursor with pH 8.0 and calcination at different conditions:

(a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.

The magnification (10,000x) is the same for all pictures.

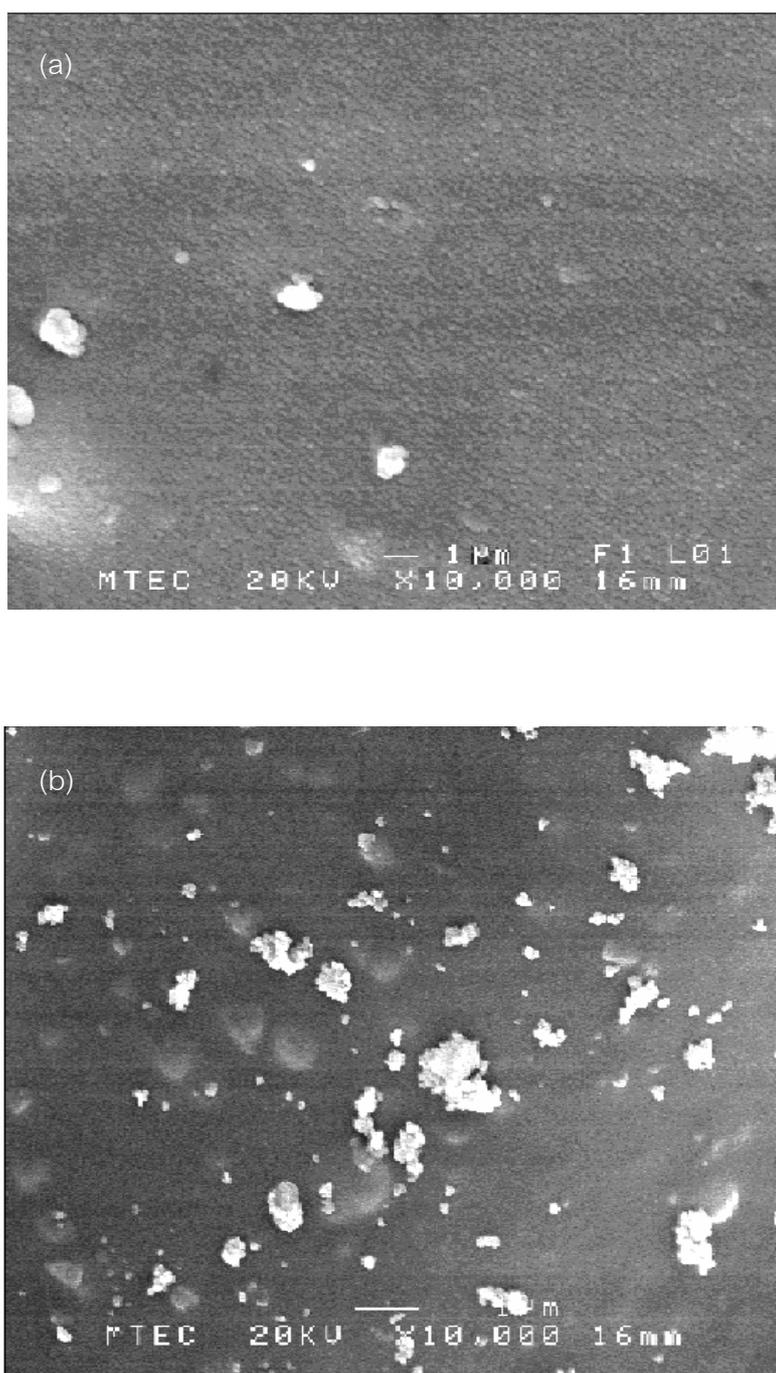


Figure 23 SEM micrographs of the NiAl_2O_4 powder obtained from gel occurring at 60°C in the system of 24.0 % (w/v) in i-propanolic solution of SPAc precursor with pH 8.0 and calcination at different conditions:

(a) 1000°C for 5 h (b) 500°C for 5 h and held at 1000°C for 5 h.

The magnification (10,000x) is the same for all pictures.

2.2.8 Comparison SEM micrographs of NiAl_2O_4 powders obtained by different preparation methods

The SEM micrographs of the resulting products obtained by different methods are compared. The SEM micrographs of the powders which prepared by a direct calcination of SPNO and SPAC exhibited a porous microstructure with irregular shaped of block-like and nonuniform particles (see Appendix F, Figure F1 and Figure F4). The more perfect particles, regular size and shape distributions with more uniform and large variations in microstructures were observed for the powders prepared via sol-gel process (see Figure 16 – 23). Thus, it could be possible to control the mechanical or physical properties of NiAl_2O_4 spinel for applying in many applications, such as industrial catalyst support. However, it is not easy to achieve such control. It is necessary to adjust the rate of hydrolysis and condensation reactions by controlling the sol-gel process parameters such as spinel precursor sources, precursor concentrations, solvents, pH values and gelation temperatures.

2.2.9 Effect of sol-gel process to physical properties of NiAl_2O_4 spinel

The valuable information obtained from SEM analysis suggested a high homogeneity of powders obtained from 1000 °C (5 h) pyrolysis of gel that occurred at room temperature, pH 8.0 for 32 % (w/v) SPNO precursor in ethanol and 16.0 % (w/v) SPAC precursor in i-propanol. Therefore, the BET surface area, pore volume and pore size of those calcined gel products are determined. The results are listed in Table 19. By comparing the surface area and porosity characteristics of NiAl_2O_4 spinel obtained via sol-gel with those directly calcined nickel aluminate precursor; it shows that these values are slightly different. The results from BET and SEM indicate that the NiAl_2O_4 powders obtained via sol-gel process have not high surface area. The reason for this result is not clear, but it is interesting to note that, because of the presence of a low surface area NiO phase in the samples (Cesteros *et al.*, 2000).

However the largest specific surface area of NiAl_2O_4 obtained from SPAC sol-gel process ($\approx 30.66 \text{ m}^2/\text{g}$) was due to its homogeneous particles distribution as seen in Figure 21 (a).

Table 19 The BET surface area, pore volume and pore size of NiAl_2O_4 spinels obtained by direct calcinations of one pot synthesis product (nickel aluminate precursor) and sol-gel process

Nickel aluminate Precursor	Method	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
SPNO	Sol-gel process	25.73	0.08	12.83
	Direct calcined	31.99	0.09	12.28
SPAc	Sol-gel process	30.66	0.08	11.03
	Direct calcined	22.58	0.04	8.97